

NOTE

Laboratory Studies of Catalysis of CO to Organics on Grain Analogs

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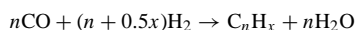
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Experiments simulating heterogeneous conversion of H₂ and CO into simple hydrocarbons in astrophysical environments have been performed, utilizing realistic cosmic grain analogs of Fe-doped silicates as Fischer–Tropsch–Type catalysts. Catalysis was studied for temperatures from 470–670 K and reactant gas mixtures of H₂/CO with a ratio of 2–100. The total gas pressure was near 0.5 bar. Maximum conversion rates of a few percentage points were achieved over a 3-h time period. Major products were methane, ethane, ethylene, carbon dioxide, and water. Products were identified by IR spectroscopy. © 2000 Academic Press

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Introduction. CO is the most abundant carbon-containing gas molecule in a variety of astrophysical environments, for instance, in interstellar regions and in the molecular cloud from which our solar system condensed. The efficiency of converting this molecule into organic compounds varies with the process. In general, homogenous gas-phase reactions are not sufficiently fast to explain the inventory of organics observed in comets and carbonaceous chondrites. One chemical mechanism which might alter the inventory of organics is a heterogeneous catalytic reaction at gas–grain surfaces, which depends on the catalytic efficiency of the grain. In natural environments this is often determined by the presence and activity of metals such as Fe or Ni. The catalytic formation of organic molecules from CO in the presence of H₂ in the nebular gas is an example of a Fischer–Tropsch–Type (FTT) reaction.



These FTT reactions are widely used in industry to produce alkanes, alkenes, and alcohols from CO and H₂ with transition metal catalysts (Hendrickson *et al.* 1970).

The possible importance of FTT synthesis of different classes of organic compounds in chondritic meteorites has long been recognized (see, e.g., Urey 1953, Hayatsu and Anders 1981, Studier *et al.* 1968). Fegley (1988) and Prinn and Fegley (1989) used an empirical rate equation, based on laboratory data, to

model the conversion rate of CO to CH₄ as a function of temperature in a nebular mixture of H₂ and CO due to FTT reactions. Kress and Tielens (1996) and Kress (1997) presented a time-dependent model for the conversion of CO to CH₄ as a function of the average number of H₂ molecules available for interaction with each metal site. In general, Kress and Tielens (1996) and Kress (1997) show that, for temperatures between 450 and 650 K, and pressures from 10^{−5} to 1 bar, the conversion from CO to CH₄ is extremely efficient in the presence of 10⁶ surface sites cm^{−3} of FeNi metal for an H₂/CO ratio of 1381. These conditions are thought to be relevant to those in the early solar nebula. The formation rate was seen to depend on the active surface area per H₂ molecule. The larger the active area, the shorter the time for conversion.

A variety of laboratory studies (Studier *et al.* 1968, Anders *et al.* 1974, Krebs *et al.* 1979) have identified the synthesis of hydrocarbons from FTT reactions of CO and H₂. Prinn and Fegley (1989) have pointed out that the conditions under which effective grain catalysis may occur are not well understood, although most laboratory data show positive results in the CO to CH₄ conversion. Experimental conditions of the studies mentioned above (0.1 to 10 bar total pressure, reaction temperatures from ~300–800 K, and H₂/CO ratios from 1 to 20) do not always reflect those thought to prevail in the nebula. Also, what constitutes an effective and relevant catalysis surface is still an open question. Experiments under a variety of temperature and pressure conditions have included catalysts such as pure iron metal, ground chondrite powder, minerals of carbonaceous chondrites (e.g., ground meteorite), or montmorillonite clay. Fegley (1998) reported conversion of CO to CH₄ under conditions reproducing the total pressure, temperatures, and C/H ratio for the jovian subnebula models. He showed that the efficiency varied with the type of catalyst but that iron metal was the most effective. Llorca and Casanova (1998) reported on a study of the synthesis of hydrocarbons along with the carbonization of the metal grains using carefully characterized FeNi metal particles supported in a high-surface-area silica aerosol under the following conditions: 5 × 10^{−4} bar, 473 K, and a ratio of H₂/CO = 250.

We present the first results of an experiment in which FTT conversion of CO to CH₄ and other organics was detected using realistic grain analogs of interstellar dust. Laboratory grain analogs condense in a cooling gas flow to a size, composition, and morphology similar to interstellar silicate dust grains formed in the cooling outflows of oxygen-rich red giant stars. The grain analogs are exposed to a gas mixture of H₂ + CO (0.4–0.6 bar, 470–770 K) with a static pressure and a temperature range within those discussed by Kress and Tielens (1996) and Kress (1997). Although H₂/CO ratios of 10³–10⁴ are typical of astronomical nebular regions, our reactant ratios varied from 2–10² to insure that the infrared absorbances of synthesized species were detectable. The various gas ratios used in our experiments, combined with the high surface area of the laboratory materials, resulted in estimated H₂/Fe site ratio of the order of

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10^{15} (see the Appendix). Except at the lowest temperatures, we detected some formation of CH_4 , C_2H_6 , and C_2H_4 in all samples after only 3 h.

Experimental. The cosmic grain analogs are Fe-doped silicate “smokes,” made in a separate high-temperature condensation chamber by combusting SiH_4 in the presence of O_2 (Nelson *et al.* 1989) and $\text{Fe}(\text{CO})_5$, followed by vapor-phase nucleation and growth in an H_2 atmosphere. Smokes have grain sizes in the range 10–30 nm (Rietmeijer and Nuth 1991). They are amorphous in morphology and composition (Rietmeijer *et al.* 1986). The small size and incomplete oxidation of the particles result from the rapid nucleation and growth. The concentration of Fe in the smoke can be controlled during production; chemical analysis of the smokes used in these experiments showed iron contents from 2–9.8% Fe by mass. Assuming the stoichiometry of the silicon component to be Si_2O_3 , these smokes have an Fe/Si number ratio from ~ 9 to 50 times lower than solar-system abundances based on meteorites (Anders and Grevesse 1989). The Fe/Si ratio in the smoke changes by less than a factor of two for reasonable alternate silicate compositions. The physical distribution of the metal within the smoke particles is not known; estimates of the site concentrations assume a uniform surface distribution proportionate to the relative numbers and ionic sizes of the various species. However, X-ray spectroscopy (discussed below) suggests that a non-uniform distribution of the iron is a possibility. Mössbauer analysis of the 2% Fe-doped silicate smoke revealed two ferric components consistent with an Fe-silica and an Fe-oxide/oxyhydroxide site and possibly a ferrous component site. The absence of magnetic field splitting, even at 15 K, is thought to be consistent with the nanophase nature of the iron particulates within the smoke. Gas adsorption (BET) measurements using CO_2 adsorbate, performed with the Micromeritics Gemini Surface Area Analyzer, indicated a total maximum surface area of $\sim 125 \text{ m}^2 \text{ g}^{-1}$ (at 195 K) for the iron silicate smokes.

A schematic diagram of the setup used for the catalytic studies is shown in Fig. 1. Approximately 0.1 g of the Fe-doped silicate smoke was packed around a porous glass dispersion tube, placed coaxially in a Pyrex glass reactor. The dispersion tube inlet and reactor outlet were attached to a vacuum manifold equipped with a diaphragm pump which circulated the gas around the closed-loop system. The reactant gas ratio of H_2/CO varied from 2–100; experimental combinations of smoke and gas mix covered a range of C/Fe ratios between 0.8 and 78. The mixture was prepared by standard manometric techniques in a separate gas handling facility. The bulb containing ~ 1 bar of the reactant gas was connected to the closed-loop system through a set of valves.

After the reactor was filled with the smoke, the vacuum manifold and glass dispersion tube were evacuated to ~ 1 Torr and the smoke was heated to 450 K under continuous vacuum pumping for 1 h to remove trapped volatiles. Then

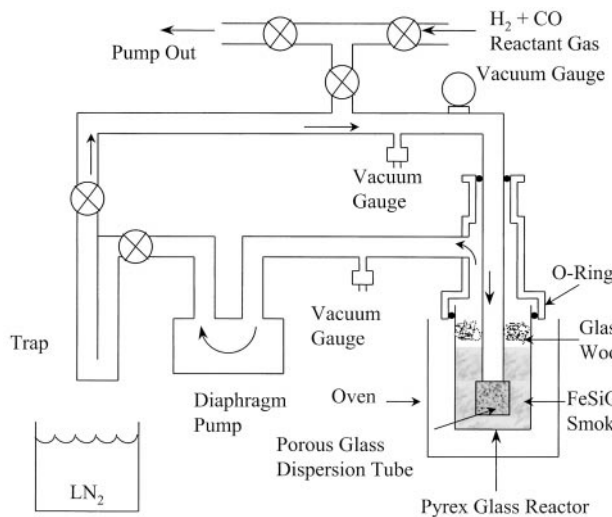


FIG. 1. Schematic diagram of the experimental apparatus used in the catalytic studies.

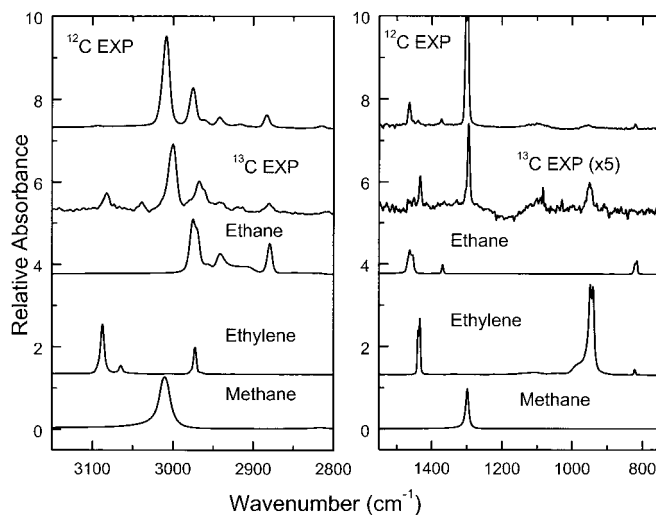


FIG. 2. The mid-infrared spectrum of an ice formed from $\text{H}_2 + {}^{12}\text{CO}$ gas mixture (${}^{12}\text{CO}/\text{H}_2 = 20$) reacted with Fe-doped silicate smoke is labeled ${}^{12}\text{C}$ EXP. Absorption features are identified by comparison with reference spectra of ${}^{12}\text{C}$ forms of ethane, ethylene, and methane mixed with water. An ice formed from $\text{H}_2 + {}^{13}\text{CO}$ gas mixture (${}^{13}\text{CO}/\text{H}_2 = 23$) reacted with Fe-doped silicate smoke is labeled ${}^{13}\text{C}$ EXP. All spectra were measured at $T \sim 20$ K.

the reactant gas mixture was admitted to the system to a pressure of ~ 0.6 bar and circulated through the closed-loop using the diaphragm pump. The entire region of the dispersion tube containing the smoke was placed into an oven and the temperature of the smoke was increased to the reaction temperature (473, 573, or 673 K) chosen for that experiment. The gas moved through the porous glass tube into the surrounding smoke, where it continued through the top of the tube and repeated its path through the loop. After the reaction period, the oven was removed and the trap section was immersed in liquid nitrogen while the diaphragm pump was running. When the reactant tube had cooled to near room temperature, the trap was valved-off and detached in order to analyze the gas as described below. A background experiment to determine the relative trapping efficiency of $\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$ (1 : 1 : 1) gases at 77 K showed a trapped ratio of (1.1 : 1 : 0.98) for gases circulated at 300 K and a trapped ratio of (1.3 : 1 : 0.93) for the same mixture after heating to ~ 600 K. Additional experiments showed no spectroscopic evidence for interconversion of the hydrocarbons in the absence of the smoke. These ratios probably represent the accumulated errors involved in the multiple steps used in the analysis.

The gas collected in the trap was condensed onto a 15 K mirror attached to the tail section of a closed-cycle cryostat. The mid-infrared ($4000\text{--}400 \text{ cm}^{-1}$) spectrum of the resulting thin ice film was used to identify new species synthesized during the reaction, by comparing it with reference spectra of CH_4 , C_2H_4 , and C_2H_6 . A complete description of the low-temperature laboratory setup used to form these ice films has been previously presented (Moore and Hudson, 1998, and references therein).

Results. Figure 2 shows a typical 20 K spectrum of the gas collected from a ${}^{12}\text{C}$ experiment (with $\text{H}_2/{}^{12}\text{CO} = 20$) compared with reference spectra of ${}^{12}\text{C}$ forms of methane, ethane, and ethylene. The $3150\text{--}2800$ and $1500\text{--}800 \text{ cm}^{-1}$ regions contain many of the “fingerprint” stretch- and bending-mode vibrations of alkane and alkene molecules. Reference spectra of a dilute mixture of these organics with water at $T < 20$ K are shown. Measured absorption coefficients for methane, ethane, and ethylene in water ice (Moore and Hudson, 1998) and the ice film thickness (determined from interference fringes) give estimated conversion yields of a few percentage points over the 3-h course of the reaction. The spectral signatures of water and carbon dioxide were also observed. Spectral regions containing these features are not shown in Fig. 2. These observations are consistent with a FTT formation mechanism. More experiments will be

necessary to determine quantitatively the amount of CO_2 and H_2O formed since the potential contribution of H_2O from any outgassing was not considered.

X-ray photoelectron spectroscopy (XPS) analysis was performed on one Fe-doped silicate smoke sample after the 3-h reaction described above, and the results were compared to an unused smoke condensed at the same time. XPS detects the elemental composition of surfaces up to 100 Å deep over a roughly circular region 300 μm in diameter. The unused smoke's carbon content in four different spots was 7, 9, 11, and 13 at.%, whereas the reacted smoke's carbon content in three different spots was 8, 9, and 25 at.%. Potential explanations for the high carbon content of the unused smokes could be residual adsorbed CO from the $\text{Fe}(\text{CO})_5$ used to synthesize the smokes or the presence of adsorbed atmospheric CO_2 on smoke surfaces. Only one of three test spots in the reacted smoke showed the increase in carbon content which would be expected with the FTT mechanism (Wentreck *et al.* 1976). Because carbon composition variations within the reacted smoke were as great as the differences between the used and unused smokes, this finding should be regarded as inconclusive, although high concentrations of catalytic sites localized on a few grains might account for the XPS results.

Because the small particle size and underoxidized nature of the smoke grains have been implicated in catalytic processes before (Moore *et al.* 1994), additional experiments were conducted to determine if our observations were the result of FTT reactions mediated by iron in the silica or if they were due to the underoxidized nature of the silicate smokes rather than to the presence of iron. A sample of SiO_x was used in the reactor and heated while 0.4 bar of a gas with an $\text{H}_2/\text{CO} \approx 2$ was circulated through it for 3 h. Amorphous SiO_x is underoxidized, but it contains no iron. To eliminate the possible reduction of the CO caused by particle size alone, in the absence of iron, another experiment using Cab-O-Sil, a commercial, fully oxidized, fumed silica of particle size similar to the silicate smokes, was completed. IR spectra of ice films formed from these experiments showed no evidence of the formation of any hydrocarbon products. The conversion of CO to CH_4 does not result from the underoxidized nature of the silicate or from the very small grain size of the catalyst: iron appears to be the key ingredient. An additional experiment was to circulate 0.4 bar of pure H_2 at 573 K through the reactor filled with Fe-doped smoke. The spectrum of the collected gas after 3 h showed only the presence of CO_2 .

Although the spectra of the smokes themselves indicated the absence of trapped or bound CO moieties remaining from the high-temperature synthesis of the smokes, there was concern that the formation of hydrocarbons occurred through reaction of H atoms with atomic carbon impurities in the solid, rather than through the catalytic reduction of CO from the gas phase. To examine that possibility, a number of experiments were conducted using various gas mixtures of H_2 with ^{13}CO (99 at.% ^{13}C ; Aldrich). The spectrum of one such experiment is shown in Fig. 2. Peaks representing $^{13}\text{CH}_4$, $^{13}\text{C}_2\text{H}_4$, and $^{13}\text{C}_2\text{H}_6$ all appear, shifted to lower frequencies compared to the identical ^{12}C peaks. The identification of the isotopic bands was confirmed by comparison to appropriate laboratory reference spectra (not shown). Under higher resolution, it is clear that some $^{12}\text{CH}_4$ is also formed in these experiments, presumably from carbon impurities in the smoke. Analysis of the methane features indicated that from 70 to 95% of total methane production was in the form of the ^{13}C isotopomer. Formation of hydrocarbons from the carbon impurity does occur to a small extent in these samples, but it is clearly not the major source of product.

Apparent reaction yields were influenced by the reaction temperature and the H_2/CO ratio of the reactant gas mix. Very low yields of CH_4 could be observed at 473 K, but the signals were sufficiently weak to preclude quantitative measurements. Gas ratios with $\text{H}_2/\text{CO} > 100$ and low total pressure presented the same problem. For that reason, quantitative results were based on experiments run at $T \geq 573$ K and gas ratios $\text{H}_2/\text{CO} \leq 25$.

Some effort was made to qualitatively assess the performance of these smokes as FTT catalysts by examining the area of the $^{13}\text{CH}_4$ peaks, normalized for iron content, smoke mass, and amount of gaseous product deposited as the ice. This quantity was monitored as a function of the total time that the smoke was exposed to the reagent gas mix at the reaction temperature. It appears that the catalytic output quickly rises after first use, goes through a maximum, and then slowly declines with continued use. This general behavior occurs for different Fe-doping levels and temperatures. The maximum occurred in the 5- to 10-h

range; production was back to the initial values after 10–25 h, depending on reaction temperature. A 2% Fe-doped smoke reacted at 573 K had the steepest curve and highest overall output; a 5% Fe-doped smoke at 673 K showed lower variation and greater longevity. The initial rise in output is probably indicative of a cleaning effect (also evident in $^{13}\text{CH}_4/^{12}\text{CH}_4$ relative production); the long tail-off probably represents slow poisoning of the catalytic sites, possibly by the carbon byproduct of catalysis. The various combinations of Fe loading, gas mixture pressure and composition, and reaction temperature represented by our data span a relatively small range of H_2/Fe values. It is not clear that our H_2/Fe estimates (see the Appendix) are accurate enough to attribute higher reaction rates to lower H_2/Fe ratios, as suggested by Kress and Tielens (1996). We may already be operating in the high-pressure (saturated) regime. Additional efforts to evaluate these materials are continuing.

These results are a first attempt at experimentally simulating the catalytic conversion of CO into hydrocarbons as it may have occurred on grains in astrophysical environments. Clearly the process is quite effective, with the detection of CH_4 , C_2H_6 , and C_2H_4 in a very short time. Efforts to further quantify these results are continuing. Variations in the initial gas ratio of H_2/CO , total gas pressure, and iron loading of the catalyst particles are planned. Such results will allow us to span the range of conditions likely in astrophysical situations, and to further evaluate the applicability of the FTT mechanism in the production of simple hydrocarbons in those environments.

Appendix. To provide a meaningful comparison of conversion rates between this work and the report of Kress and Tielens (1996), we attempted to model our Fe-doped silicate grain system in the same physical context as their work, i.e., a grain in a 1- cm^3 volume whose surface contains a number of catalytic sites, exposed to a gas mixture. Temperature and pressure were fixed to correspond to our experimental values. Utilizing the average diameter of the silicate smoke particles (~ 30 nm), the measured BET surface area ($125 \text{ m}^2 \text{ g}^{-1}$), and the 10% Fe loading of some of the smokes, and assuming a density equivalent to that of Cab-O-Sil fumed amorphous silica (0.048 g cm^{-3}) which has comparable grain size, we estimated the number of iron sites on a sample of silicate smoke that would have a total surface area equivalent to the single FeNi grain of Kress and Tielens (1996). That surface-equivalent silicate smoke sample, maintained in a 1- cm^3 volume at 0.4 bar pressure (with $\text{H}_2/\text{CO} = 20$) at 600 K, had $\log(\text{H}_2/\text{Fe site}) = 15.3$. Using a polynomial fitted to the data appearing in Fig. 2 of Kress and Tielens (1996), we calculate that it takes nearly 10^6 year to convert 10% of the CO into an organic. Due to numerous approximations, these values must be considered crude, but they do indicate the realistic iron-doped silicate grains can effect conversion on time scales comparable to metallic grains, despite the significantly lower density of surface sites.

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